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(71) Applicant: Océ-Nederland B.V.
5914 CC Venlo (NL)

(72) Inventors:
- Tazelaar, Frans Willem
5912 HR Venlo (NL)
- Markies, Peter Richard
5971 DP Grubbenvorst (NL)
- Van den Reek, Johannes Adrianus
5644 KA Eindhoven (NL)
- Van der Stappen, Cornelis Johannes Maria
6524 HE Nijmegen (NL)

(74) Representative: Hanneman, Henri W.A.M. et al
Océ-Nederland B.V.
Patents and Information
St. Urbanusweg 43
P.O. Box 101
5900 MA Venlo (NL)

(54) Lengthened difunctional perfluoropolyether oils and rubbers prepared therewith

(57) The invention relates to a difunctional perfluoro-polyether oil, prepared by reacting a perfluoropolyether diol oil having a weight averaged molecular weight (Mw) between 1500 and 3000 with a chain lengthener from the group of diacid chlorides and diisocyanates, and to perfluoropolyether rubbers prepared by means of these chain-lengthened oils.

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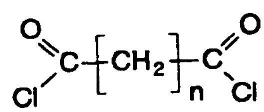
Description

The invention relates to difunctional perfluoro-polyether oils and rubbers prepared by means of such oils. Oils of this kind are known from D Sianesi, Organofluorine Chemistry 1995, page 435. The properties of perfluoropolyether oils are very favourable for use as oils, lubricants in car waxes, and so on. The functional oils are suitable as an intermediate product in the preparation of rubbers, release coatings and the like. One disadvantage, however, is that these oils have a relatively low molecular weight and this restricts their range of application.

The object of the invention is to provide difunctional perfluoropolyether diols via a simple synthesis route with much higher molecular weights. To this end, lower molecular difunctional perfluoropolyether diols are lengthened with a chain lengthener chosen from the group of diisocyanates and diacid chlorides.

In one embodiment of the invention, the diisocyanate chain lengthener used is a difunctional diisocyanate perfluoropolyether oil. The resulting difunctional perfluoropolyether oils may have OH or NCO terminal groups depending on the diol: diisocyanate ratio. Starting with molecular weights of 2000 - 2500 for the starting diol and the starting diisocyanate, it is a simple matter to obtain molecular weights of chain-lengthened perfluoropolyether oils of about 6000 to about 25000.

In another embodiment of the invention, the diacid chloride used is



where n = 0 - 4 and the chain lengthener used is preferably glutaryl dichloride. Starting with a molecular weight of between 2000 and 2500 of the starting diol, it is possible to obtain molecular weights of between 4000 and 25000 for chain-lengthened perfluoropolyether oils.

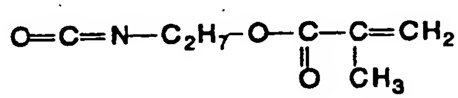
After cross-linking to form a rubber, these lengthened difunctional perfluoropolyether oils are very suitable as top layer rubber, e.g. in fixing devices in hot roll fusers, as top layer rubber on an intermediate medium as described in EP 0 581 355, as abhesive coatings, release coatings, and so on. After curing they are also suitable as anti-wetting coatings for nozzle plates of inkjet printheads.

This cross-linking can be carried out in various ways. One of the ways is so to derivatise the functional terminal groups of the chains that curing becomes possible possible under the influence of light, heat and/or moisture.

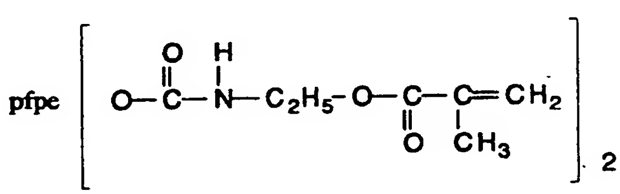
In a first embodiment of the method for the rubber cross-linking, the OH-groups of a chain-lengthened perfluoropolyether do are esterified with an acryloyl chloride.

Cross-linking then takes place with UV light in the presence of a photo-initiator at higher temperatures. Cross-linking can also be effected by heating in the presence of a peroxide.

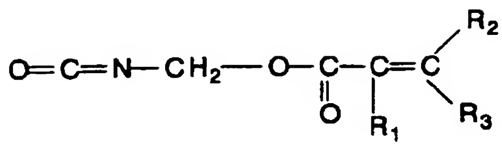
In a second embodiment of the method for rubber cross-linking, the OH groups in a chain-lengthened perfluoropolyether diol HO-pfpe-OH are converted with a urethane acrylate compound, such as



to perfluoropolyether



For this, isocyanate acrylates according to the molecular formula



where p = 1 - 5 and R_1, R_2 and R_3 can be jointly and independently chosen from H and a lower alkyl group, chosen from the group methyl, ethyl, n-propyl, isopropyl, n-butyl, and t-butyl.
Cross-linking then takes place in the same way as in the first embodiment.

Suitable catalysts for the curing of urethane perfluoropolyethers are dibutyl tin dilaurate, dibutyl tin oxide, various iron derivatives such as ferroacetyl acetonate, tertiary amines etc, in quantities from 0.001 to 2 % by weight. Perfluoropolyethers with (meth)acrylate or urethane (meth)acrylate terminal groups can be cross-linked

1) with the aid of peroxides such as dibenzoyl peroxide, 2,5-bis(ter-butylperoxy)-2,5-dimethylhexane, ter-butylperoxybenzate, benzophenone, etc in quantities from 0.1 to 3 % by weight in combination with heat (> 100°C) and
2) with the aid of photo-initiators such as α,α-diethoxyacetophenone, o-nitrobenzene diazonium hexafluoroantimonate, fluorenone, triphenyl amines, benzoin alkyl ethers, carbazole, etc, in combination with UV light.

Acrylate reactive perfluoropolyethers according to the invention are very suitable as an additive to improve surface properties (non-wetting, antistatic) in UV or EB (electron beam) curing coatings based on various acrylates or methacrylates. There are applications in the area of paper coatings, coating of plastics and glass articles and the like.

In a third embodiment, the OH groups of a chain-lengthened perfluoropolyether diol are converted with

$$O{=}C{=}N{-}\left[CH_2\right]_3{-}Si\left[OEt\right]_3$$

to perfluoropolyether

$$\left[-O-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{N}-\left[CH_2\right]_3-Si\left[OEt\right]_3\right]_2$$

In general compounds from the group

$$O{=}C{=}N{-}\left[CH_2\right]_q{-}Si\left[OR\right]_3$$

where q = 1-4 and R chosen from the group methyl, ethyl, n-propyl and i-propyl, can be used.
Cross-linking then takes place under the influence of a catalyst such as tin octoate with water and with temperature elevation. It is a simple matter to cure these rubbers in air. One of the particular advantages of these transparent rubbers is the good conductivity. A thin layer of perfluoropolyether rubber according to the invention charges up barely if at all, even after long periods of charging (up to 1 kV).

It has surprisingly been found that the prepared perfluoropolyethers as described above with -NH-C(O)-sequences in the terminal group, such as triethoxysilyl and urethane acrylate, preferably chain-lengthened with a coupler giving rise to C = 0 - or other polar groups in the main chain, exhibit a surface resistance of the order of magnitude of 10^8 - 10^9 Ωcm. This is a factor 100 - 1000 lower than the surface resistance of perfluoro-polyethers based on urethane cross-linking (10^{12} Ωcm) and various other unfilled elastomers, such as (fluoro)- silicone rubber. This property makes the lay-

ers based on the said perfluoropolyethers intrinsically antistatic.

Although we do not wish to speculate about the conducting mechanism in the perfluoropolyethers layers, a possible explanation can be sought in the presence of ions in the product, caused by the various steps in the preparation, by which a form of ion-conductivity can arise in the layer.

Control of this ion-conductivity in perfluoropolyether products (oils and rubbers) can be done via two mechanisms: via variation of the molecular structure, so via the introduction of polar relaxation mechanisms using polar groups, for example by the introduction of polyethylene oxide groups in the polymer chains and via the addition and variation of various ions, such as quaternary ammonium salts and lithium salts to the perfluoropolyether matrix.

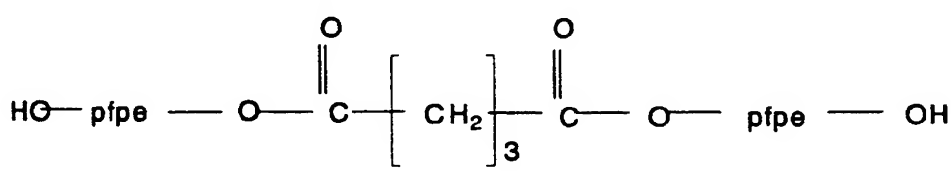
Possible applications are in the area of using these layers as transparent top layers on intermediates as described in EP 0 581 355, transparent conductive toner coatings, transparent non-stick coatings on photoconductors and other image-forming media, as indicated, for example, in US 5 319 334, on transport rollers and the like. Other possible applications where transparency and conductivity are necessary are, for example, in the motor vehicle industry, the carpet industry, and optical instruments.

In order further to improve the mechanical properties, it is possible to cross-link mixtures of chain-lengthened perfluoropolyether oils provided with reactive groups. The elastic properties and tearing strength can be controlled by correct choice of the reactants.

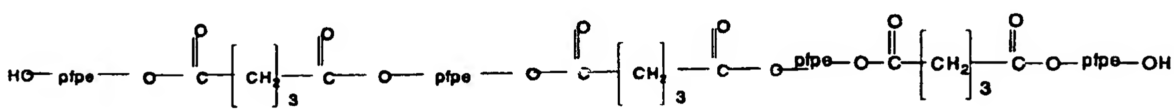
The invention will now be described in greater detail with reference to a number of examples.

Example 1

Chain lengthening of lower molecular OH terminated perfluoropolyether oils was performed as follows in a 3-neck flask provided with a top agitator, dropping funnel (with gas circulation) and a spherical condenser. The flask was continuously washed with nitrogen. 500 g of OH terminated perfluoropolyether oil, HO-perfluoropolyether-OH, with a mass averaged molecular weight, MW = approximately 2150 g/mol were weighed into the 3-neck flask. 10.2 g of glutaryl dichloride was added dropwise in 1 hour via the dropping funnel with agitation at 0°C. After 24 hours at 100°C a viscous substantially clear light orange liquid was obtained. This oil



can be converted to rubber in the same way as in Example 2. The above reaction can also be repeated by reacting the product of the reaction with glutaryl dichloride again under the same conditions. The result



is the formation of:

This compound theoretically has an MW of about 8900 g/mol. In practice, MWs of 6500 (100°C, 24 hours) and 11000 (160°C, 24 hours), can be found depending on the reaction temperature. This oil can also be further extended in the same way by again reacting the product for 24 hours at 100°C with glutaryl dichloride. In this way an OH terminated perfluoropolyether oil was synthesised with an MW of 11000 and with an MW of 25000 g/mol in the case of reaction at 160°C.

All these oils can be converted to a rubber in the same way as in Example 2.

Example 2

98.1 g (11.2 mmol) of perfluoropolyether diol (HO-perfluoropolyether-OH) 25 g of 1,1,2 trifluorotrichloroethane and 5 g of triethylamine were cooled in an ice bath to 0°C in a 250 ml 4-neck flask provided with an agitator, nitrogen inlet, a closed dropping funnel (with gas circulation) and a spherical condenser. 3 g (33.1 mmol) of acryloyl chloride

$$CH_2{=}CH{-}C({=}O)Cl$$

was dissolved in 40 g of 1,1,2 trifluorotrichloro-ethane in the dropping funnel. This solution was added dropwise with agitation to the mixture in the 4-neck flask. The resulting white-yellow dispersion was kept at 55°C for 1 hour, whereupon 50 ml of ethanol was added. The resulting strongly yellow mixture was then agitated for 15 minutes at 50°C whereupon it was cooled. The acrylate-terminated oil obtained in this way was washed with a 1,1,2 trifluorotrichloro-ethane/ethanol mixture. After evaporation of the solvents, 87 g (yield 88%) of a clear light-brown acrylate terminated oil remained:

$$H_2C{=}C(H){-}C({=}O){-}O{-}\mathrm{pfpe}{-}O{-}C({=}O){-}C(H){=}CH_2$$

This oil was mixed with a photo-initiator, 20 µl of 2,2 diethoxyacetophenone per 10 g of acrylate terminated oil.

This mixture was applied as a top layer to a metal cylinder provided with an approximately 20 mm thick layer of peroxide hardened silicone rubber. The approximately 60 µm thick top layer was then cured in a nitrogen atmosphere by means of a UV lamp. The resulting clear rubber is strong and elastic. The glass transition temperature of the rubber is about -125°C.

Example 3

Chain lengthening on the basis of a urethane reaction was carried out in a 250 ml reaction vessel with a top agitator, nitrogen inlet and a thermometer. 50.6 g of OCN-perfluoropolyether'-NCO with an Mw of 2562 g/mol, 89.3 g of HO-perfluoropolyetherII-OH with an Mw of 2258 g/mol and 1.5 g of 1 Mn catalyst solution 1 W% solution (dibutyl tin dilaurate in 1,1,2 trichloro-trifluoroethane) were reacted together. This reaction mixture was heated for 1 hour at 75°C under nitrogen. The resulting lengthened perfluoropolyether oil

$$HO{-}\mathrm{pfpe}{-}O{-}C({=}O){-}N(H){-}\mathrm{pfpe}^{I}{-}N(H){-}C({=}O){-}O{-}\mathrm{pfpe}^{II}{-}OH$$

was then provided with acrylate end groups via the method of Example 1. By means of benzoyl peroxide and heat, the oil provided with 2.5% carbon black was finally converted to a top layer rubber. The mixture with benzoyl peroxide was for this purpose placed in a layer about 60 µm thick on a substrate. The layer was then cured at a temperature of about 140°C.

Example 4

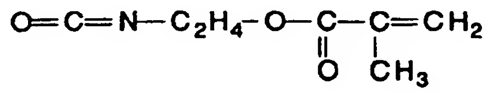
A rubber was made in the same way as in Example 3, an 80:20 mixture of
a perfluoropolyether HO - pfpe - OH,
and a perfluoropolyether tetraol
being used as perfluoropolyether diol.

$$CH_2OH{-}CH[OH]{-}H_2C{-}O{-}CH_2{-}F_2C{-}\mathrm{pfpe}{-}CF_2CH_2{-}O{-}CH_2CH[OH]{-}CH_2OCH$$

The presence of the tetraol perfluoropolyether increased the cross-link density after cross-linking with, for example, acrylate groups in the resulting rubber, so that the rubber hardness was increased.

Example 5

184.1 g of perfluoropolyether diol with an Mw of about 2200, 19.55 g of 2-isocyanatoethyl methacrylate



and 0.11 g of dibutyl dilaurate were stirred for 4½ hours at room temperature in a 3-neck flask with a condenser, agitator and nitrogen inlet. The resulting product was worked up with 1,1,2 trifluorotrichloro-ethane and stirred with 20 µl of diethoxyacetophenone per 10 g of perfluoropolyether oil. The product was then cured in one operation in a nitrogen atmosphere by means of a UV lamp (UV-C: wavelength about 360 nm).

After about 15 minutes a well-cured clear antistatic rubber was obtained.

Example 6

61.85 g of chain-lengthened perfluoropolyether diol according to Example 2 with an Mw of about 11000, 2.95 g of 3-(triethoxysilyl) propylisocyanate and 0.65 g of catalyst solution (1 w% dibutyl tin dilaurate in tetrahydrofuran) was agitated at room temperature for 15 hours. NMR analysis of the resulting clear oil showed that the OH groups of the chain-lengthened perfluoropolyether diol were completely converted.

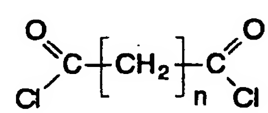
The oil was then mixed with 1 w% tin octate. The resulting mixture was applied in a layer approximately 60 µm thick to a fabric belt provided with about 2.5 mm peroxide hardened silicone rubber. This perfluoropoly-ether layer was air cured for about 4 hours. The resulting non-stick clear rubber had good visco-elastic properties.

Claims

1. Difunctional perfluoropolyether oil, characterised in that the oil is prepared by reacting a perfluoropolyether diol oil having a weight averaged molecular weight (mw) between 1500 and 3000 with a chain lengthener from the group of diacid chlorides and diisocyanates.

2. Difunctional perfluoropolyether oil according to claim 1, characterised in that the diisocyanate used is a difunctional diisocyanate perfluoropolyether oil.

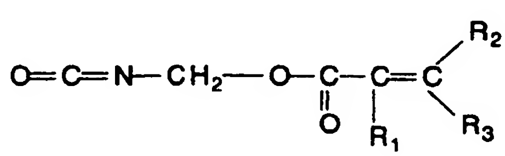
3. Difunctional perfluoropolyether oil according to claim 1, characterised in that the chain lengthener used is a diacid chloride having the molecular formula



where n = 0 - 4.

4. Difunctional perfluoropolyether oil according to claim 3, characterised in that the diacid chloride used is glutaryl dichloride.

5. Perfluoropolyether rubber, characterised in that the rubber is prepared from derivatised perfluoropolyether diol oil chain-lengthened according to any of claims 1 to 4, wherein the OH terminal groups are derivatised with a compound from the group of acryloyl chlorides, isocyanate acrylates according to the molecular formula



where p = 1 - 5 and R_1, R_2 and R_3 can be jointly and independently chosen from H and a lower alkyl group, chosen from the group methyl, ethyl, n-propyl, isopropyl, n-butyl, and t-butyl or with a compound from the group

$$O{=}C{=}N{-}\left[CH_2\right]_q{-}Si\left[OR_4\right]_3$$

where q = 1 - 4 and R_4 can be chosen from the group methyl, ethyl, n-propyl and i-propyl, whereafter these derivatised perfluoropolyether oils are cross-linked under the influence of a suitable catalyst.

6. Perfluoropolyether rubber according claim 4 characterized in that said rubber is prepared using as derivatized perfluoropolyether diol oil having a surface resistance of approximately 10^8-10^9 Ωcm.

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EUROPEAN SEARCH REPORT

Application Number
EP 96 20 2894

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US 4 933 408 A (GOLDENBERG MERRILL) 12 June 1990 * claim 1 * * column 4, line 41 - line 68 * * column 5, line 34 - line 54 * * column 7, line 49 - line 62 * ---	1,2	C08G18/50 C08F20/28 C08F20/36 C08G63/682 C08G65/00
X	EP 0 621 298 A (AUSIMONT SPA) 26 October 1994 * claims 1,4-9 * * page 3, line 6 - line 33 * * example 1 * ---	1,2	
A	EP 0 322 624 A (SIEMENS AG) 5 July 1989 * claims 1-3 * * page 2, line 12 - line 39 * ---	1	
A	EP 0 622 391 A (AUSIMONT SPA) 2 November 1994 * claims 1-3,6 * * page 3, line 8 - page 4, line 6 * -----	1	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

C08G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	19 February 1997	Van Puymbroeck, M

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

Océ-Technologies B.V., of Venlo

CROSS-LINKABLE COMPOUNDS COMPRISING A PERFLUOROPOLYETHER MOIETY

This non-provisional application claims priority under 35 U.S.C. 119(a) on European Patent Application No. 02078182.9, filed in the European Patent Office on July 26, 2002, the contents of which are hereby incorporated by reference.

The invention pertains to a cross-linkable compound comprising a perfluoropolyether (PFPE) moiety which is ultimately terminated by an oxygen atom and bonded through a spacer attached to the said oxygen atom with an ethylenically unsaturated group. The invention further pertains to a perfluoropolyether rubber obtainable by hydrosilating said cross-linkable compound and to an apparatus for transferring a toner image from an image-forming medium to a receiving medium comprising said perfluoropolyether rubber.

Cross-linkable compounds comprising PFPE are known in the art, for instance from US Pat. No. 4,565,714 that describes a low surface energy material that is a hydrosilation reaction product of a compound containing fluorine and aliphatic unsaturation with a compound containing silicon-bonded hydrogen. Such compositions can be cured to a low surface energy material that in coating form is effective as a release surface for use with the most aggressive class of adhesives known in the art or for other applications requiring low adhesion. These compounds have a linking group that connects the unsaturation with the polymer and is, for example, selected from esters, amides, urethanes, and ethers such as $-CH_2-O-$, $-CH_2-NH-(C=O)-$, $-CH_2-NH(C=O)-O-$, and $-(CH_2)-[-(CH_2)-]N(C=O)-$, wherein the unsaturation is vinyl ($-CH=CH_2$) or an alkyl or phenyl substituted derivative thereof. The present invention pertains to compounds that are derived from PFPE moieties that are hydroxy-terminated, commonly known as hydroxy-terminated PFPE-oils. These hydroxy-terminated PFPE oils can be easily coupled, through reaction with the hydroxy group, to an ethylenically unsaturated group as known in the art. This leads to the compound as worded in the above introduction. These compounds appear to be particularly useful for anti-stick purposes. For instance, methylol-terminated perfluoropolyethers can serve as a basis for making the compounds to which the present invention pertains. These PFPE compounds are

disclosed as intermediates to other monomers and are prepared by reduction of esters, e.g., by reaction with lithium aluminum hydride or sodium borohydride. Reaction of these alcohols with ethylenically unsaturated halides, e.g., allyl bromide, in the presence of sodium hydride or potassium hydroxide provides ethylenically unsaturated PFPE's. It was, however, found that the known low surface energy materials deteriorate after a couple of months, especially when used at elevated temperatures, leading to loss of their non-sticking properties. This phenomenon is especially undesired when the rubber is applied in top layers of apparatuses for transferring a toner image from an image-forming medium to a receiving medium.

Apparatuses for transferring a toner image from an image-forming medium to a receiving medium are known, for instance from US Pat. No. 5,742,889, which is incorporated by reference. The top layer in such apparatus is provided with a rubber that is obtained form reacting PFPE oil with a chain lengthener. However, the rubbers disclosed in this patent do not show the desired non-sticking properties after a number of months at elevated working temperatures.

It is therefore an objective of the present invention to provide a perfluoropolyether (PFPE) oil that can be used for making perfluoropolyether rubbers, that are particularly suitable for use in top layers of apparatuses for transferring a toner image from an image-forming medium to a receiving medium, and that preserve their non-sticking properties for much longer times at elevated temperatures.

It has now been surprisingly found that this objective, and other objectives for obtaining suitable rubbers, such as good visco-elastic properties including high elasticity and low compression set, is met with the above cross-linkable compounds when the spacer extends over at least three atoms between the oxygen atom and the ethylenically unsaturated group. Thus, the "distance" between the oxygen atom which terminates the compound comprising the PFPE-moiety and the ethylenically unsaturated group involves at least three atoms in a row. As a result, good monomers for providing suitable rubbers can be obtained.

In one embodiment, the spacer extends over at least four atoms. It has been found that this embodiment can provide monomers that lead to even better rubbers.

In another embodiment, the atoms of the spacer are carbon atoms. This surprisingly leads to rubber materials having better anti-stick properties.

Yet another embodiment pertains to compounds having the formula:
$D-(C_nF_{2n}O)_m-Q-B-A$, wherein
A stands for an ethylenically unsaturated group of the formula $HR_1C=CR_2R_3$, wherein R_1 is selected from H, alkyl, phenyl, alkyl-substituted phenyl and aralkyl; R_2 is selected from H, alkyl, phenyl, alkyl-substituted phenyl and aralkyl, and R_3 is a bond or $Si(R_4)_2$, R_4 being independently H or alkyl;
B stands for a hydrocarbyl or fluorocarbylspacer extending over at least three carbon atoms;
$(C_nF_{2n}O)_m$ is the PFPE moiety wherein n is independently an integer of 1 to 4 and m is an integer of 2 to 500;
Q is a group selected from CF_2-CH_2-O, CH_2-CH_2-O; and
D stands for $HO-CH_2CF_2-O-$ or A-B-Q-O-, wherein n, A, B, and Q have the previously given meanings.

In the above definition, "alkyl" is preferably a branched or unbranched alkyl group with 1 to 4 carbon atoms, such as methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, sec-butyl and the like. The alkyl group in the substituted phenyl preferably has the same meaning. The term “aralkyl” means an aryl substituted alkyl group, wherein the branched or unbranched alkyl group preferably has 1 to 6 carbon atoms and the aryl group preferably is phenyl.

In the formula $(C_nF_{2n}O)_m$ for the PFPE moiety, "n" is independently selected. Thus, this formula includes both homopolymers (wherein the values “n” are the same for each recurring monomeric unit) and co-polymers, wherein the PFPE moiety is built up of different recurring monomers with different values of “n”, for instance PFPE moieties that are built from both (CF_2O) and (CF_2CF_2O) recurring units. Preferably, the PFPE moiety has a molecular weight of about 1,000 to 20,000. Thus, preferably, dependent on the molecular weight of the monomeric units, m is preferably between 4 and 300. Such PFPE moieties are known in the art, for instance from US Pat. Appln. No. 2001/0008916 A1, which is incorporated by reference.

The above compounds can be hydrosilated by bringing about a condensation of a silicon-hydrogen-containing compound with the ethylenically unsaturated PFPE compound, preferably in the presence of a hydrosilating catalyst.
"Hydrosilation" means a reaction involving the addition of a silicon-hydrogen group across a pair of aliphatic unsaturated carbon atoms, i.e., carbon atoms joined by double bonds. The reaction can be illustrated by the following general equation:
$\equiv$Si-H + C=C $\Rightarrow$ $\equiv$Si-C-CH.

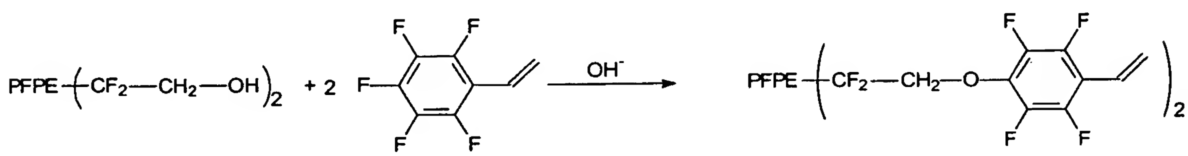
"Perfluoropolyether" ("PFPE") in the sense of the invention means a polyether, i.e. a compound comprising a chain of at least two alkoxy groups. The alkylene groups, which can be branched or are straight chains are completely, or at least to a substantial extent, fluorinated. The PFPE might occasionally comprise alkylene groups which are not completely fluorinated. In particular embodiments, the alkylene groups contain 1 to 6, preferably 1 to 4, carbon atoms but the invention is not restricted to such groups.

The hydrosilation catalysts employed in the compositions of the present invention include all of the well-known metal-containing catalysts, which are effective for catalyzing a hydrosilation reaction between silicon-bonded hydrogen groups and ethylenically unsaturated groups. These materials include, for example, the finely divided platinum catalysts, such as those described in U.S. Pat. No. 2,970,150, the chloroplatinic acid catalysts described in U.S. Pat. No. 2,823,218, the platinum hydrocarbon complexes taught in U.S. Pat. Nos. 3,159,601 and 3,159,662 as well as the platinum alcoholate catalysts described in U.S. Pat. No. 3,220,972, the platinum complexes having an ultraviolet displaceable group such as are disclosed in U.S. Pat. No. 4,530,879 and the (cyclopentadienyl)(trialiphatic)platinum complexes such as are disclosed in U.S. Pat. No. 4,510,094. In addition, the platinum chloride-olefin complexes described in U.S. Pat. No. 3,416,946 are useful herein. A suitable catalyst is a platinum catalyst solution of ABCR, SIP 6832 in a concentration of 3 to 50 ppm on a weight basis. All of the teachings of hydrosilation catalysts in the aforesaid U.S. patents are incorporated herein by reference.

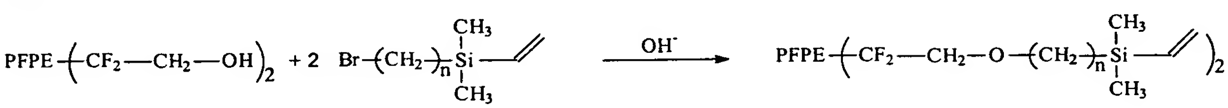
The composition of the invention can also contain other ingredients such as hydrosilation inhibitors, dyes, pigments and reinforcing fillers, e.g., carbon black, fumed silica, titanium dioxide, etc. Furthermore, the release character of the cured composition can be modified, i.e., the value of the force required to separate an adhesive from the surface of the cured composition can be modified by any method known in the art, e.g.,

by the method described previously, by the addition to the composition of 0.1 to 10 parts of a release modifier per 100 parts of the composition, or by use of different primers. Preferably, the release modification provides a differential release of at least 10 percent. Such modifiers are known and include, for example, tetraalkoxyalkyl silicates such as $Si(OC_2H_4OC_2H_5)_4$, such as are described in U.S. Pat. No. 3,518,325; graft polymers having a polyorganosiloxane segment and an organic polymer segment as are described in U.S. Pat. No. 4,366,286; vinyl terminated diorganopolysiloxanes in which 3 to 39 mole percent of the diorgano units are non-terminal diphenylsiloxane units; and the three-dimensional toluene soluble silicate resins, known in the silicate art as MQ resins which are described in U.S. Pat. Nos. 2,676,182 and 2,857,356.

Suitable cross-linkable compounds according to the invention can be made, for instance, as follows:



and



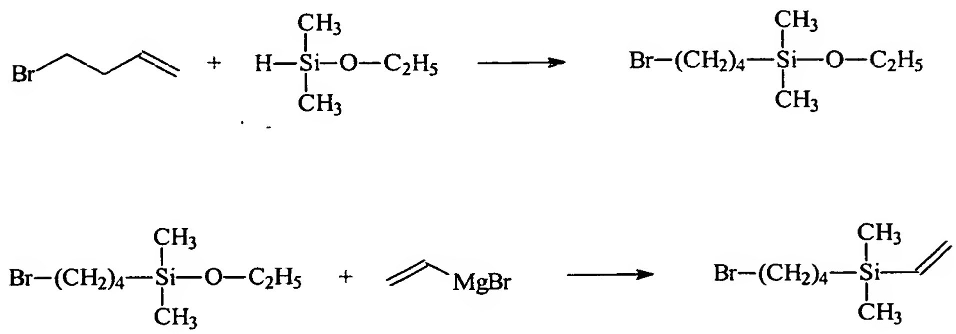
(n = 3)

whereas from the prior art it is known to make a cross-linkable compound for instance as follows:

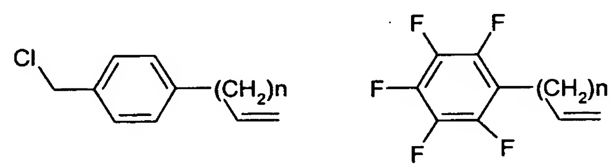
$$PFPE\text{-}(CF_2\text{-}CH_2\text{-}OH)_2 + 2\ Br\text{-}CH_2\text{-}CH{=}CH_2 \xrightarrow{OH^-} PFPE\text{-}(CF_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH{=}CH_2)_2$$

In these formulae, PFPE represents any PFPE as indicated above. In the first example of an embodiment according to the invention, the spacer extends over 4 carbon atoms (between the ultimate oxygen atom and the ethylenically unsaturated group). In the second example the spacer extends over 3 carbon atoms + 1 silicon atom. It has been found that a spacer extending over at least three atoms, in particular carbon atoms, between the oxygen atom and the silicon atom, lead to excellent rubbers. The prior art shows a spacer extending over 1 carbon atom.

The above silylalkylbromide intermediate compound is novel and can be made according to the following scheme (for example when n=4):



End groups that can very suitably be coupled to a hydroxy group of the linking group are, for instance,



n = 0 or 1

The unsaturated bond of these end groups can be hydrosilated (vulcanization) with a multi-SiH cross-linker to form a silylated compound with a spacer between the unsaturated group (vinyl) and the oxygen atom of the linking group of at least 3 carbon atoms to obtain a stable bond.

Suitable SiH cross-linkers are methyl tris(dimethylsiloxy)silane ['T(Mh)3'], cyclo(tetramethyltetrasiloxane) and homologs thereof ['(Dh)x'], short linear siloxane derivatives ['M(Dh)nM'], tetrakis(dimethylsiloxy)silane ['Q(Mh)4'] and higher oligomers thereof ['Qn(Mh)m'],

To the vinyl terminated PFPE oil is added subsequently an inhibitor for obtaining sufficient pot life for good processing. A suitable inhibitor is 1-ethynylcyclohexanol ['ECH'] in a weight ratio of 500-5000 ppm relative to the oil. The inhibitor is injected pure in melted form using a microliter syringe.

A SiH cross-linker is added in an amount of 1.5 – 3 equivalents of SiH groups with regard to the vinyl groups in the PFPE oil. If necessary for a better mixability, a quantity of a solvent may be added, for instance, 1,3-bis(trifluormethyl)benzene ['fluoroxylene'].

After completion of mixing, a hydrosilation catalyst is added, in a concentration of about 5 – 50 ppm.

After mixing, for instance with a mechanical stirrer, and degassing by evacuation, the mixture can be cross-linked (cured) in the air (coatings) or, when no solvent is used, in a mold at 120-140°C. Curing usually takes 1 – 10 minutes. Further curing may take place in the air overnight at 120°C. The hardness then further increases due to evaporation of the solvent, oxidation and coupling of excess SiH groups.

It is also possible to apply a pre-curing of part of the PFPE oil with excess of SiH cross-linker (about 2-5 moles of SiH cross-linker per vinyl group). This is particularly useful when the mixing of PFPE oil and SiH cross-linker is insufficient. Pre-curing is for instance performed at 120°C for 0.5 h under nitrogen atmosphere in 1,3-bis(trifluorobenzene) as solvent. The 'alloy' of PFPE oil with SiH reactive silicones is obtained after evaporation of the solvent and can be stored under nitrogen.

When this reagent is strongly opaque and a silicone fraction separates, an effective separation can be achieved by extraction with low-molecular PFPE solvent ['HT 70'] and cyclohexane. A mixture of crude pre-cured product and 1 part of PFPE solvent can be separated from a silicon fraction by extraction with 1 part of cyclohexane.

The invention also relates to an apparatus for transferring a toner image from an image-forming medium to a receiving medium comprising:

an endless movable intermediate medium including a support provided with a top layer secured to the support via a rear surface, the intermediate medium being in contact with the image-forming medium in a first transfer zone;

heating means for heating the toner image on the top layer of the intermediate medium;

a biasing means for contacting the intermediate medium in a second transfer zone; and

transport means for transporting the receiving medium through the second transfer zone, wherein the top layer comprises a perfluoropolyether rubber which is obtainable by hydrosilating a cross-linkable compound comprising a perfluoropolyether (PFPE) moiety which is ultimately terminated by an oxygen atom and bonded through a spacer attached to the said oxygen atom with an ethylenically unsaturated group, wherein the

spacer extends over at least three atoms between the oxygen atom and the ethylenically unsaturated group.

The invention is further illustrated with the following non-limitative examples.

Example 1

4-Bromobutyl-dimethyl-ethoxysilane

800 g of 4-bromo-1-butene were reacted with 15% excess of dimethylethoxysilane (939 ml). In a 2 l reactor 0.5 g of $Ru_3(CO)_{12}$ and 800 ml of 4-bromo-1-butene were brought under nitrogen and 939 ml of dimethylethoxysilane were added under nitrogen and the mixture was brought at 65°C. After 0.5 h the bath temperature was raised to 80°C and the mixture was allowed to react overnight. After distillation 1329 g (93.7%) of 4-bromobutyl-dimethyl-ethoxysilane were isolated.

4-Bromobutyl-dimethyl-vinylsilane

A 3 l reactor was charged under nitrogen with 1 l of vinyl magnesium bromide in THF (tetrahydrofuran) and 184 g of 4-bromobutyl-dimethyl-ethoxysilane were added slowly at room temperature. The mixture was then refluxed at 70°C for 16 h. After cooling on ice, the mixture was quenched with 407 g of a 20% HBr (w/w) solution, after which it was stirred for another 1.5 h. The THF layers were separated from the aqueous layers and neutralized with aq. sodium hydrogen carbonate solution. The THF was evaporated and the residue was distilled in the presence of 1 g Pt/C to obtain 135.8 g (79.8%) of pure 4-bromobutyl-dimethyl-vinylsilane

Example 2

Coupling of 4-bromobutyl-dimethyl-vinylsilane to PFPE-oil

A 1 l reactor was charged with 200 g (91 mmole) of OH-terminated PFPE-oil (Fluorlink D, from Ausimont s.p.a.), 220 ml of 1,3-bis(trifluoromethyl)benzene and 48.2 g (218 mmole) of 4-bromobutyl-dimethyl-vinylsilane. The mixture was heated at 70°C under stirring until a clear colorless solution was obtained, after which a mixture of 43.3 g of a 47% KOH solution, 160 ml of water and 8 g of tetrabutylammonium hydroxide was added dropwise. After reacting for 4 h at 100°C, the aqueous layer was separated after which a fresh mixture of 43.3 g of a 47% KOH solution, 160 ml of water and 8 g of tetrabutylammonium hydroxide were added and stirred for another 16 h at 100°C. The

mixture was cooled down and the water layer was separated. The reaction mixture was washed with water, glacial acetic acid and methanol. The oily residue was concentrated and stirred with 15 g of polyvinylpyridine and 100 ml of HT™70 (a non-reactive PFPE-oil with a boiling point of 70°C, from Ausimont s.p.a.) for 3 days. After filtering and evaporation to dryness, a colorless oil was obtained, more than 99% of which was coupled to the end group

The invention being thus described, it will be obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure from the spirit and scope of the invention, and all such modifications as would be obvious to one skilled in the art are intended to be included within the scope of the following claims.

CLAIMS

1. A cross-linkable compound comprising a perfluoropolyether (PFPE) moiety which is ultimately terminated by an oxygen atom and bonded through a spacer attached to the said oxygen atom with an ethylenically unsaturated group, wherein the spacer extends over at least three atoms between the oxygen atom and the ethylenically unsaturated group.

2. A compound according to claim 1, wherein the spacer extends over at least four atoms.

3. A compound according to claim 1 or claim 2, wherein the atoms of the spacer are carbon atoms.

4. The cross-linkable compound of claim 1 or claim 2, having the formula:
$D\text{-}(C_nF_{2n}O)_m\text{-}Q\text{-}B\text{-}A$, wherein
A stands for an ethylenically unsaturated group of the formula $HR_1C{=}CR_2R_3$, wherein R_1 is selected from H, alkyl, phenyl, alkyl-substituted phenyl and aralkyl; R_2 is selected from H, alkyl, phenyl, alkyl-substituted phenyl and aralkyl and R_3 is a bond or $Si(R_4)_2$, R_4 being independently H or alkyl;
B stands for a hydrocarbyl or fluorocarbyl spacer extending over at least three carbon atoms;
$(C_nF_{2n}O)_m$ is the PFPE moiety wherein n is independently an integer of 1 to 4 and m is an integer of 2 to 500;
Q stands for a terminating group selected from $CF_2\text{-}CH_2\text{-}O$ and $CH_2\text{-}CH_2\text{-}O$ and
D stands for $HO\text{-}CH_2CF_2\text{-}O\text{-}$ or A-B-Q-O-, wherein n, A, B, and Q have the previously given meanings.

5. The cross-linkable compound of claim 4 wherein the hydrocarbyl spacer extends over at least four carbon atoms.

6. The cross-linkable compound of claim 4 wherein A stands for $H_2C{=}CH\text{-}$.

7. The cross-linkable compound of claim 4 wherein D is A-B-Q-O-, Q stands for CF_2-CH_2-O-, and B-A has the formula -C_6F_4-CH=CH_2 or -$(CH_2)_o$-Si$(CH_3)_2$-CH=CH_2, wherein o is 3 or 4.

8. A process for preparing the cross-linkable compound of claim 1 comprising reacting a hydroxy-terminated perfluoropolyether (PFPE) compound with a compound of the formula A-B-Hal, wherein A is an ethylenically unsaturated group, B is a spacer which extends over at least three atoms and Hal is F, Cl, Br or I.

9. A process according to claim 8, wherein A stands for an ethylenically unsaturated group of the formula HR_1C=CR_2R_3, wherein R_1 is selected from H, alkyl, phenyl, alkyl-substituted phenyl and aralkyl; R_2 is selected from H, alkyl, phenyl, alkyl-substituted phenyl and aralkyl and R_3 is a bond or Si$(R_4)_2$, R_4 being independently H or alkyl; and B stands for a hydrocarbyl or fluorocarbyl spacer extending over at least three carbon atoms.

10. A perfluoropolyether rubber obtainable by hydrosilating the cross-linkable compound of claim 1.

11. An apparatus for transferring a toner image from an image-forming medium to a receiving medium comprising:
an endless movable intermediate medium including a support provided with a top layer secured to the support via a rear surface, the intermediate medium being in contact with the image-forming medium in a first transfer zone;
heating means for heating the toner image on the top layer of the intermediate medium;
a biasing means for contacting the intermediate medium in a second transfer zone; and
transport means for transporting the receiving medium through the second transfer zone, wherein the top layer comprises the perfluoropolyether rubber of claim 10.

ABSTRACT

The invention pertains to a cross-linkable compound comprising a perfluoropolyether (PFPE) moiety derived from an hydroxy-terminated PFPE-oil, which is bonded through a spacer with an ethylenically unsaturated group, wherein the spacer extends over at least three carbon atoms. The invention further relates to a perfluoropolyether rubber obtainable by hydrosilating said cross-linkable compound and to an apparatus for transferring a toner image from an image-forming medium to a receiving medium.

Attorney Docket No. 0142-0419P

BIRCH, STEWART, KOLASCH & BIRCH, LLP

P.O. Box 747 • Falls Church, Virginia 22040-0747
Telephone: (703) 205-8000 • Facsimile: (703) 205-8050

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COMBINED DECLARATION AND POWER OF ATTORNEY FOR PATENT AND DESIGN APPLICATIONS

As a below named inventor, I hereby declare that my residence, post office address and citizenship are as stated next to my name; that I verily believe that I am the original, first and sole inventor (if only one inventor is named below) or an original, first and joint inventor (if plural inventors are named below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

Insert Title: CROSS-LINKABLE COMPOUNDS COMPRISING A PERFLUOROPOLYETHER MOIETY

Fill in Appropriate Information - For Use Without Specification Attached:

the specification of which is attached hereto. If not attached hereto, the application is identified by the attorney docket number as set forth above and/or the following:
The specification was filed on ______ as
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and amended on ______ (if applicable) and/or
the specification was filed on ______ as PCT
International Application Number ______; and was
amended on ______ (if applicable)

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

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Insert Priority Information: (if appropriate)

Prior Foreign Application(s) — Priority Claimed

(Number)	(Country)	(Month/Day/Year Filed)	Yes	No
02078182.9	EPO	July 26, 2002	☒	☐
			☐	☐
			☐	☐
			☐	☐

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(Application Number)	(Filing Date)

All Foreign Applications, if any, for any Patent or Inventor's Certificate Filed More than 12 Months (6 Months for Designs) Prior to the Filing Date of This Application:

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Country	Application Number	Date of Filing (Month/Day/Year)

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Insert Prior U.S. Application(s): (if any)

(Application Number)	(Filing Date)	(Status - patented, pending, abandoned)

Attorney Docket No. 0142-0419P

I hereby appoint the practitioners at CUSTOMER NO. 2292 as my attorneys or agents to prosecute this application and/or an international application based on this application and to transact all business in the United States Patent and Trademark Office connected therewith and in connection with the resulting patent based on instructions received from the entity who first sent the application papers to the practitioners, unless the inventor(s) or assignee provides said practitioners with a written notice to the contrary:

Send Correspondence to:

BIRCH, STEWART, KOLASCH & BIRCH, LLP or CUSTOMER NO. 2292
P.O. Box 747 • Falls Church, Virginia 22040-0747
Telephone: (703) 205-8000 • Facsimile: (703) 205-8050

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Full Name of First or Sole Inventor; Insert Name of Inventor; Insert Date This Document is Signed

GIVEN NAME/FAMILY NAME	INVENTOR'S SIGNATURE	DATE*
CORNELISSEN, Ronald Hubert Carlos	[signature]	7-22-2003
Residence (City, State & Country): Helmond		CITIZENSHIP: The Netherlands
MAILING ADDRESS (Complete Street Address including City, State & Country): Luchtvaartplein 36, 5703 HJ Helmond, The Netherlands		

Insert Residence; Insert Citizenship; Insert Post Office Address

Full Name of Second Inventor, if any: see above

GIVEN NAME/FAMILY NAME	INVENTOR'S SIGNATURE	DATE*
VAN ZEEVENTER, Karel Pieter Daniël	[signature]	7-22-03
Residence (City, State & Country): Grashoek		CITIZENSHIP: The Netherlands
MAILING ADDRESS (Complete Street Address including City, State & Country): Roomweg 17, 5985 NR Grashoek, The Netherlands		

Full Name of Third Inventor, if any: see above

GIVEN NAME/FAMILY NAME	INVENTOR'S SIGNATURE	DATE*
MARKIES, Peter Richard	[signature]	7-22-2003
Residence (City, State & Country): Grubbenvorst		CITIZENSHIP: The Netherlands
MAILING ADDRESS (Complete Street Address including City, State & Country): Ericaplein 32, 5971 GC Grubbenvorst, The Netherlands		

Full Name of Fourth Inventor, if any: see above

GIVEN NAME/FAMILY NAME	INVENTOR'S SIGNATURE	DATE*
VERBEEK, Guy Peter Maria	[signature]	7-22-2003
Residence (City, State & Country): Maaseik		CITIZENSHIP: Belgian
MAILING ADDRESS (Complete Street Address including City, State & Country): Eikerstraat 78/7, B-3680 Maaseik, Belgium		

Full Name of Fifth Inventor, if any: see above

GIVEN NAME/FAMILY NAME	INVENTOR'S SIGNATURE	DATE*
VERBUNT, Joannes Adrianus	[signature]	7-23-2003
Residence (City, State & Country): Velden		CITIZENSHIP: The Netherlands
MAILING ADDRESS (Complete Street Address including City, State & Country): Heideweg 39, 5941 AW Velden, The Netherlands		

Full Name of Sixth Inventor, if any: see above

GIVEN NAME/FAMILY NAME	INVENTOR'S SIGNATURE	DATE*
DE JONG, Sandra Mei-ling	[signature]	7-22-2003
Residence (City, State & Country): Venlo		CITIZENSHIP: The Netherlands
MAILING ADDRESS (Complete Street Address including City, State & Country): Harry Meijerstraat 127, 5913 RG Venlo, The Netherlands		

*DATE OF SIGNATURE

Attorney Docket No. 0142-0419P

Full Name of Seventh Inventor, if any: see above

GIVEN NAME/FAMILY NAME ZEELEN, Peter Maria Cornelis	INVENTOR'S SIGNATURE	DATE* 7-22-03
Residence (City, State & Country) Maasbree		CITIZENSHIP The Netherlands
MAILING ADDRESS (Complete Street Address including City, State & Country) Zandberg 22, 5993 AA Maasbree, The Netherlands		

*DATE OF SIGNATURE